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Using density functional theory to study shape-reactivity relationships in Keggin Al-nanoclusters

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ABSTRACT

Keggin-based aluminum nanoclusters have been shown to be efficient sorbents for the removal of arsenic from water. Obtaining a molecular-level understanding of the adsorption processes associated with these molecules is of fundamental importance, and could pave the way for rational design strategies for water treatment. Due to their size and the availability of experimental crystal structures, Al nanoclusters are computationally tractable at the density functional theory (DFT) level. Here, we compare the reactivity of three aluminum polycations: $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ (Al$_{13}$), $[Al_{30}O_8(OH)_{56}(H_2O)_{26}]^{18+}$ (Al$_{30}$), and $[Al_{32}O_8(OH)_{60}(H_2O)_{30}]^{20+}$ (Al$_{32}$). We use DFT calculations to determine reactivity as a function of particle topography, using sulfate and chloride as adsorption probes. Our comparative modeling of outer-sphere adsorption of Cl$^-$ and SO$_4^{2-}$ on Al$_{13}$, Al$_{30}$, and A1$_{32}$ supports that the unique "hourglass" shape characteristic to Al$_{30}$ gives rise to relatively strong adsorption in the molecular beltway, as well as a wide range of reaction energies as a function of particle topography.

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1. Introduction

Al-based materials are known to exhibit high reactivity towards polyoxoanion species such as arsenate, and therefore are frequently used in coagulation-coprecipitation and adsorption-based water remediation. Studies point to the utility of the Keggin-based aluminum hydroxide nanocluster $[Al_{30}O_8(OH)_{56}(H_2O)_{26}]^{18+}$ (Al$_{30}$) in the efficient removal of arsenic from water. Mertens et al. have been prime investigators in researching the removal of inorganic sodium arsenate from contaminated water samples (Mertens et al., 2012a). In a recent study, the reactivity of several Al-based sorbents was compared by measuring the uptake capacity of arsenic, specifically As(V) (Mertens et al., 2016). The materials tested included Al$_{30}$ solution, Al$_{30}$ enriched polyaluminum chloride (PACl$_{30}$), polyaluminum granulate (PAG), and the natural Al mineral phase, gibbsite. The pure Al$_{30}$ and PACl$_{30}$ showed similar As uptake efficiency, suggesting that the Al$_{30}$ content of PACl$_{30}$ is responsible for its reactivity towards the contaminant. All of the nanocluster sorbents adsorbed at least 93% of arsenic from solutions of initial arsenic concentration ranging from 0.133 to 0.667 mmol/L, while the gibbsite sample only decreased the As(V) concentration by 50%.

While Al nanoclusters can adsorb contaminants at a variety of pH conditions it has been shown that PACl$_{30}$ efficiency is highest near neutral pH, making it an excellent candidate for the purification of natural waters (Mertens et al., 2012a, 2012b; Mertens, 2011).

Conceptually, the high reactivity of the Al$_{30}$ molecule has been rationalized through structure-reactivity relationships that were developed for extended mineral surfaces and based on Pauling's rules of inorganic crystal stability (Pauling, 1929). Mineral-water interfaces are well-defined models for geochemical systems. Surface energetics for mineral-water interfaces have been extracted experimentally, but it is time consuming and relative to UHV conditions (Israelachvili and Adams, 1978; Jordan and Geiger, 2014). Theoretical studies using methods such as DFT and *ab initio* molecular dynamics (AIMD) can help to fill in the conceptual gap between macroscopic experiments and molecular understanding. However, information from atomistic modeling currently trails the information obtained from over a decade of experimental studies of hydrated single-crystal surfaces (see, for example, Catalano et al. (2008), Fenter et al. (2000), Fenter and Sturchio (2004), Eng et al. (2000), Catalano (2010), Rosso et al. (2010), Abadia et al. (2014)). In the absence of more robust chemical modeling, bond-valence theory has been a popular and useful means of mapping experimental information about adsorption to structure-property relationships. The bond-valence model as formulated by Brown relates bond length to bond strength through the bond valence *s* of

atom type i (Brown, 2009). The model is parameterized such that the sum over s_i for each atom should equal its formal valence, where $s_i = (R/R_0)^{-N}$, R is the observed bond length while R_0 and N are fitted bond valence parameters. The conceptual result born out of bond-valence theory is that functional group type is a key predictor of mineral surface reactivity (Hiemstra et al., 1989). In a recent review, Brown and Calas (2011) discuss the oxygen functional groups exposed as "long-term docking stations". They explain that the formation of (partially covalent) inner-sphere (IS) adsorption complexes immobilizes the adsorbate. On the other hand, outer-sphere (OS) adsorption is considered to be relatively weak on mineral-water interfaces. Here, when were refer to an OS adsorption complex involving an Al Keggin molecule, we specifically mean that no ligand exchange occurs between the Al of the Keggin and the adsorbate. Conventionally, the interaction between the adsorbate and the Keggin would be thought to be weaker in an OS complex than in an IS complex.

It is easy to see why, in conjunction with high reactivity noted in the literature, the importance of functional group number and type is assumed to govern the reactivity of Al nanoclusters. The Al_{13} molecule has two types of exposed doubly bridging ligands (μ_2-OH) and twelve equivalent bound water molecules (η-H_2O). Al_{30} and Al_{32} are comprised of two δ-Al_{13} Keggin units, $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ (Al_{13}) connected by four Al linkers (Abeysinghe et al., 2012, 2013a). There are three surface functional group categories in the Al_{30} and Al_{32} molecule − bound water molecules (η-H_2O), doubly bridging ligands (μ_2-OH), and triply-bridging ligands (μ_3-OH) (Rustad, 2005; Casey, 2006; Casey and Rustad, 2007; Sun et al., 2011). The Al_{32} molecule contains two additional Al atoms on the Al_{30} molecule but contains the same types of oxygen functional groups. Indeed, the existence of numerous distinct functional groups on the surface of the Al Keggin molecules has been highlighted as an argument for adopting these species as geochemical models (Casey and Rustad, 2007; Casey, 2006).

The Keggin structural motif common to the Al nanoclusters studied here is of general interest to a wide range of chemistry beyond adsorption. For example, Furrer et al. has studied aluminum flocs and have found that the Al flocculants that precipitate from streams contain a significant amount of $Al(O)_4$, which is the building blocks of the ε-Al_{13} Keggin (Furrer et al., 2002). The ferrihydrite structure of Michel et al. based on pair distribution function analysis exhibits similarities to the δ-Keggin structure (Michel et al., 2010). More recently, an α-Keggin Fe_{13} cluster was characterized by Sadeghi et al., providing further evidence that the growth of both natural and synthetic phases proceeds by aggregation of clusters (Sadeghi et al., 2015). The Keggin motif in prenucleation clusters has also been observed in Nb-polyoxometalate systems (Hou et al., 2013). Other aspects of the reactivity of Keggin clusters have been shown to depend on composition. For example, Rustad and Casey have determined heteroatom substitution can impact the kinetics of ligand exchange reactions (Rustad and Casey, 2012; Rustad et al., 2004; Reusser et al., 2014). These examples of broad interest in Keggin clusters provides further motivation for modeling studies aimed at assigning their reactivity to underlying physical properties.

In our previous work, we carried out DFT calculations to rationalize the crystal structure of an Al_{30} Keggin species with two surface-bound Cu^{2+}, referred to as Cu_2Al_{30}−S (Abeysinghe et al., 2013b). The crystallization was done in the presence of disulfonate ions (2,6-NDS), and the structure exhibited Cu^{2+} bound to Al_{30} in a corner-sharing bidentate fashion, while the sulfonate groups had an OS relationship to the molecule. DFT modeling of IS Cu^{2+} adsorption and/or OS SO_4^{2-} adsorption (as a simplified approximation to the bulky 2,6-NDS counter ions used in the experiment)

was carried out. When Cu^{2+} and SO_4^{2-} adsorption was considered separately, the cation and anion showed opposite trends in adsorption site preference as a function of location on the particle surface. Specifically, Cu^{2+} adsorption was preferred at the ends or "caps" of the molecule, while SO_4^{2-} adsorption was preferred in the molecular center or "beltway" region. Furthermore, while OS adsorption is generally thought of as a weak interaction, the reaction energies associated with the OS adsorption of SO_4^{2-} were relatively large. When co-adsorption was modeled, the preferred structure had both Cu^{2+} and SO_4^{2-} adsorbed in the beltway, congruent with the crystal structure and suggested that the strong OS adsorption controlled the coadsorption site preference. The variation in the Cu^{2+} and SO_4^{2-} adsorption energies as a function of molecular topography, specifically between the beltway and caps, was greater than 1 eV per ion, despite the fact that all of the inner-sphere adsorption geometries involved two η-H_2O groups. These results suggest that reactivity factors other than oxygen functional group identity were governing the DFT energy trends. Plots of the electrostatic potential (V_{el}) mapped onto the charge density of the molecule revealed that the unique "hourglass" shape of Al_{30} gives rise to more positive values in the beltway and less positive values at the caps. The reason for this variation is attributed to how the topography of the particle surface affects the distribution of η-H_2O functional groups. In the former, SO_4^{2-} can only interact with the oxygen functional groups directly beneath it, while in the latter the SO_4^{2-} can interact with a larger area of the Al_{30} surface.

In the present work, we aim to directly assess how shape affects adsorption trends on Al_{13}, Al_{30}, and Al_{32}, using DFT calculations and AIMD. We model OS adsorption of SO_4^{2-} and Cl^- to sample the potential energy surfaces of the three Al nanoclusters. SO_4^{2-} and Cl^- are chosen as representative probe adsorbates based on their common use in crystallization experiments. Additionally, these ions allow us to compare reactivity trends as a function of adsorbate size and charge, and can be considered an analog for contaminant polyoxoanions such as selenate and molybdate. These different ions all have a different ionic radii and this could lead to a more complete discussion of how the size of the ion effects reactivity.

2. Computational and theoretical methods

AIMD simulations and DFT geometry optimizations are carried out using the DMol^3 package developed by Delley (Delley, 1990, 2000), with aqueous effects accounted for by the conductor-like screening model (COSMO) (Klamt and Schüürmann, 1993). The AIMD trajectories are used to search for minimum energy adsorption configurations, which allows for a better sampling of the potential energy surface than through static DFT calculations alone. AIMD simulations were carried out in the (N,V,T) ensemble with trajectories of 1000 steps of 0.463 fs. The temperature was set at 330 ± 2 K and controlled by using the Nosé-Hoover chain (NHC) (Nose, 1984; Hoover, 1985) method. A temperature higher than normal environmental conditions was intentionally chosen to give the system additional thermal energy such that more of the potential energy surface would be accessible to the adsorbate. The lowest energy configurations from the AIMD simulations were then subjected to geometry optimization at the DFT level, and all of the reported energetics in this study are from those DFT results. An additional reason to consider higher temperature in a system with many bound water groups is the fact that the GGA style exchange correlation functional used in our calculations has been shown to over-structure water (Leung et al., 2006). The inversion symmetry of Al_{30} and Al_{32} is maintained in the adsorbed systems by modeling two anions with atomic coordinates that are also related by inversion symmetry.